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FABRIC CARE COMPOSITIONS

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Field of the invention

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The present invention relates to a fabric care compositions and more particularly to a method and a composition which exhibit reduced or even no formation of scum on the fabrics and/or the washing machine parts whilst still providing care to the colors of fabrics treated therewith.

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Background of the invention

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The appearance of colored fabrics, e.g., clothing, bedding, household fabrics like table linens is one of the areas of concern to consumers. Indeed, upon typical consumer's uses of the fabrics such as wearing, washing, rinsing and/or tumble-drying of fabrics, a loss in the fabric appearance; which is at least partly due to loss of color fidelity and color definition, is observed. Such a problem of color loss is even more acute after multiwash cycles.

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It is therefore an object of the invention to provide a composition which provides improved color care to the laundered fabrics, especially after multiwash cycles.

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Dye fixing components as described in EP462806 are suitable components for this purpose. Indeed, these components provide care to the color of fabrics by assisting in binding the loosely held dye to the fabric.

- 5 Still, a new class of materials, namely, the amino-functional polymers, can also be used. Indeed, these have recently found increasing use in the treatment of fabric in order to provide care to the color of fabrics.

- 10 However, a problem now encountered with compositions comprising such dye fixing agent and/or amino-functional polymer is the resulting scum which forms on the treated fabrics and/or the washing machine parts.

- 15 Not to be bound by theory, it is believed that the formation of scum arises from the interaction of such nitrogen containing compounds, i.e. the amino-functional polymers and/or the dye fixing agent, with the anionic species like anionic surfactants that are carried over from the detergent, especially over multiple wash cycles. This interaction results into insoluble, sticky precipitates on the fabrics and/or the washing machine parts.

- 20 Accordingly, the formulator of a fabric care composition is faced with the dual challenge of formulating a composition which exhibit reduced or even no formation of scum but without being detrimental to the colors of the treated fabrics.

- 25 The Applicant has now surprisingly found that the provision of a scum reducing agent selected from a water-soluble cationic surface active agent; a polyoxyalkylene alkyl amine surface active agent, and mixtures thereof, to compositions comprising a nitrogen containing compound selected from an amino-functional polymer, a dye fixing agent and mixtures thereof, overcomes
30 the problem.

Summary of the invention

The present invention relates to a fabric care composition comprising

i)- a nitrogen containing compound selected from a polyamino-functional polymer, a dye fixing agent, and mixtures thereof, and

5 ii)- a scum reducing agent selected from a water-soluble cationic surface active agent; a polyoxyalkylene alkyl amine surface active agent, and mixtures thereof; with the proviso that when the sole nitrogen containing compound is a polyamino-functional polymer, the polymer is present in amounts greater than 1% by weight.

10 In another aspect of the present invention, there is provided the use of surface active agent in a composition comprising a nitrogen containing compound selected from a polyamino-functional polymer, a dye fixing agent, and mixtures thereof, for reducing or preventing the formation of scum on fabrics or washing machine parts contacted with the composition.

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Detailed description of the invention

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According to one aspect of the invention, there is provided a fabric care composition with effective and durable color care properties.

25 An essential component of the invention is a nitrogen containing compound selected from an amino-functional polymer, a dye fixing agent, and mixtures thereof.

Amino-functional polymer

30 The amino-functional polymer advantageously provides care to the colors of fabrics.

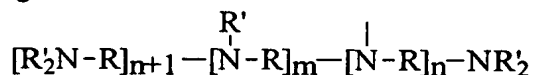
35 The amino-functional polymers of the present invention are water-soluble or dispersible, polyamines. Typically, the amino-functional polymers for use herein have a molecular weight between 200 and 10^6 , preferably between 600 and 20,000, most preferably between 1000 and 10,000. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also

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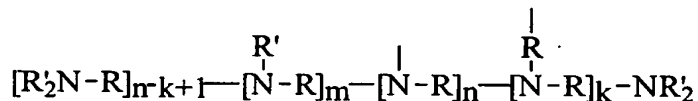
comprise polyamine branching chains to a greater or lesser degree. Preferably, the polyamine backbones described herein are modified in such a manner that at least one, preferably each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

For the purposes of the present invention the term "modification" as it relates to the chemical structure of the polyamines is defined as replacing a backbone -NH hydrogen atom by an R' unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an R' unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution is preferably accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the amino-functional polymer have the general formula:



The cyclic polyamine backbones that comprise the amino-functional polymer have the general formula:



The above backbones prior to optional but preferred subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure



is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified

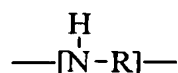
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subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

- 10 In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



- 15 is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

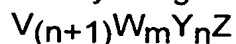
- 20 In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure



- is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.
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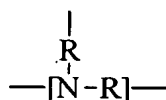
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



for linear amino-functional polymer and by the general formula



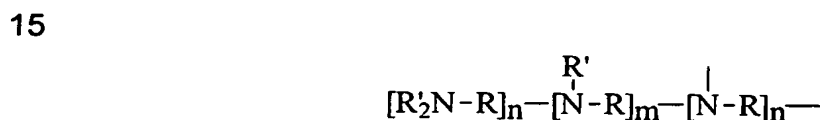
for cyclic amino-functional polymer. For the case of polyamines comprising rings, a Y' unit of the formula



10 serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula



therefore comprising no Z terminal unit and having the formula



20 wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula



that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 2 to 700, preferably 4 to 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

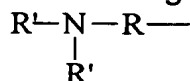
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Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one

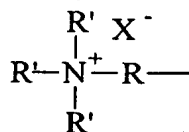
- of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, Y' or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is
- 5 unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units or Y' units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

Modified primary amine moieties are defined as V "terminal" units having one of three forms:

- 10 a) simple substituted units having the structure:

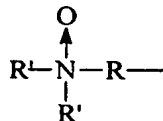


- b) quaternized units having the structure:



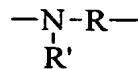
wherein X is a suitable counter ion providing charge balance; and

- 15 c) oxidized units having the structure:



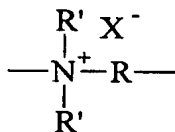
Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

- a) simple substituted units having the structure:



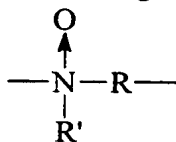
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- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

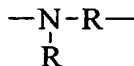


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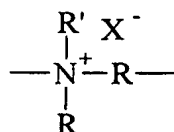
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Other modified secondary amine moieties are defined as Y' units having one of three forms:

- a) simple substituted units having the structure:

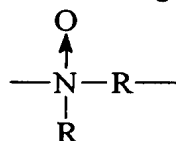


- 5 b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

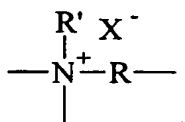


Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

- a) unmodified units having the structure:

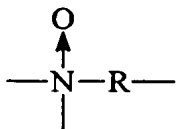


- 15 b) quaternized units having the structure:



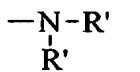
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

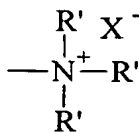


Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

- a) simple substituted units having the structure:

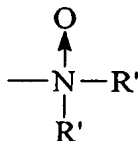


- 25 b) quaternized units having the structure:



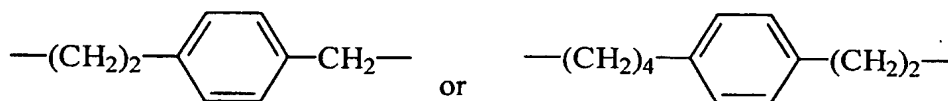
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:



- 5 When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for R'. For example, a primary amine unit comprising one R' unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula (HOCH₂CH₂)HN-.
- 10 For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH₂. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted
- 15 with any of the R' units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore R' cannot be a hydrogen.
- 20 The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene wherein the hydroxyl moiety may take any
- 25 position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C₄-C₁₂ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C₈-C₁₂ dialkylarylene which for the purpose of the present invention are arylene
- 30 moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula

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although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C₂-C₁₂ alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise - (R¹O)_xR⁵(OR¹)_x-, -CH₂CH(OR²)CH₂O)_z(R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -CH₂CH(OR²)CH₂-, -(R¹O)_xR¹-, and mixtures thereof. Preferred R units are selected from the group consisting of C₂-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -CH₂CH(OR²)CH₂-, -(CH₂CH(OH)CH₂O)_z(R¹O)_yR¹(OCH₂CH-(OH)CH₂)_w-, - (R¹O)_xR⁵(OR¹)_x-, more preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxy-alkylene, C₄-C₁₂ dihydroxyalkylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, -(CH₂CH(OH)CH₂O)_z(R¹O)_yR¹(OCH₂CH-(OH)CH₂)_w-, and mixtures thereof, even more preferred R units are C₂-C₁₂ alkylene, C₃ hydroxyalkylene, and mixtures thereof, most preferred are C₂-C₆ alkylene. The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

R¹ units are C₂-C₆ alkylene, and mixtures thereof, preferably ethylene.

R² is hydrogen, and -(R¹O)_xB, preferably hydrogen.

R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkylene, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof, preferably C₁-C₁₂ alkyl, C₇-C₁₂ arylalkylene, more preferably C₁-C₁₂ alkyl, most preferably methyl. R³ units serve as part of R' units described herein below.

R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, preferably C₁-C₁₀ alkylene, C₈-C₁₂ arylalkylene, more preferably C₂-C₈ alkylene, most preferably ethylene or butylene.

R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -C(O)(R⁴)_rC(O)-, -R¹(OR¹)-, -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-, -C(O)(R⁴)_rC(O)-, -CH₂CH(OH)CH₂-, R⁵ is preferably ethylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -

$R^1(OR^1)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, more preferably $-CH_2CH(OH)CH_2-$.

R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene.

- 5 The preferred "oxy" R units are further defined in terms of the R^1 , R^2 , and R^5 units. Preferred "oxy" R units comprise the preferred R^1 , R^2 , and R^5 units. The preferred cotton soil release agents of the present invention comprise at least 50% R^1 units that are ethylene. Preferred R^1 , R^2 , and R^5 units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

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i) Substituting more preferred R^5 into $-(CH_2CH_2O)_xR^5(OCH_2CH_2)_x-$ yields $-(CH_2CH_2O)_xCH_2CHOHCH_2(OCH_2CH_2)_x-$.

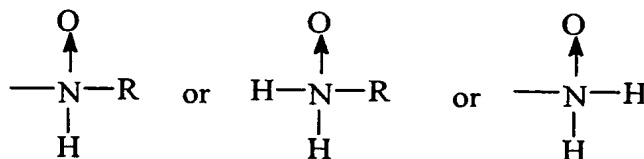
15 ii) Substituting preferred R^1 and R^2 into $-(CH_2CH(OR^2)CH_2O)_z-(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w-$ yields $-(CH_2CH(OH)CH_2O)_z-(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w-$.

iii) Substituting preferred R^2 into $-CH_2CH(OR^2)CH_2-$ yields $-CH_2CH(OH)CH_2-$.

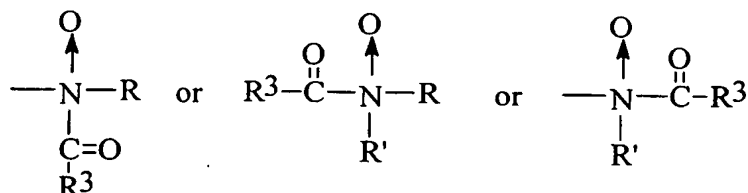
R' units are selected from the group consisting of hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_mB$, $-C(O)R^3$, preferably hydrogen, C_2-C_{22} hydroxyalkylene, benzyl, C_1-C_{22} alkylene, $-(R^1O)_mB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, more preferably C_1-C_{22} alkylene, $-(R^1O)_xB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, most preferably C_1-C_{22} alkylene, $-(R^1O)_xB$, and $-C(O)R^3$. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing R' . A most preferred R' unit is $(R^1O)_xB$.

25 R' units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:

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Additionally, R' units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the R' unit -C(O)R³ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

B is hydrogen, C₁-C₆ alkyl, -(CH₂)_qSO₃M, -(CH₂)_pCO₂M, -(CH₂)_q-(CHSO₃M)CH₂SO₃M, -(CH₂)_q(CHSO₂M)CH₂SO₃M, -(CH₂)_pPO₃M, -PO₃M, preferably hydrogen, -(CH₂)_qSO₃M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q-(CHSO₂M)CH₂SO₃M, more preferably hydrogen or -(CH₂)_qSO₃M.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies -(CH₂)_pCO₂M, and -(CH₂)_qSO₃M, thereby resulting in -(CH₂)_pCO₂Na, and -(CH₂)_qSO₃Na moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a -(CH₂)_pPO₃M moiety substituted with sodium atoms has the formula -(CH₂)_pPO₃Na₃. Divalent cations such as calcium (Ca²⁺) or magnesium (Mg²⁺) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl⁻), bromine (Br⁻) and iodine (I⁻) or X can be any negatively charged radical such as sulfate (SO₄²⁻) and methosulfate (CH₃SO₃⁻).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; m has

the value from 2 to 700, preferably from 4 to 400, n has the value from 0 to 350, preferably from 0 to 200; m + n has the value of at least 5.

Preferably x has a value lying in the range of from 1 to 20, preferably from 1 to 10.

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The preferred amino-functional polymers of the present invention comprise polyamine backbones wherein less than 50% of the R groups comprise "oxy" R units, preferably less than 20% , more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

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The most preferred amino-functional polymers which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C₂-C₁₂ alkylene, preferred is C₂-C₃ alkylene, most preferred is ethylene.

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The amino-functional polymers of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

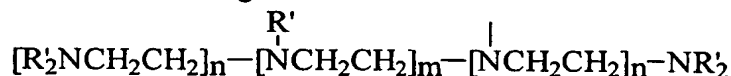
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For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone.

Preferred amino-functional polymers of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneimines (PAI's), preferably polyethyleneimines (PEI's), or PEI's connected by moieties having longer R units than the parent PAI's or PEI's.

Preferred amine polymer backbones comprise R units that are C₂ alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



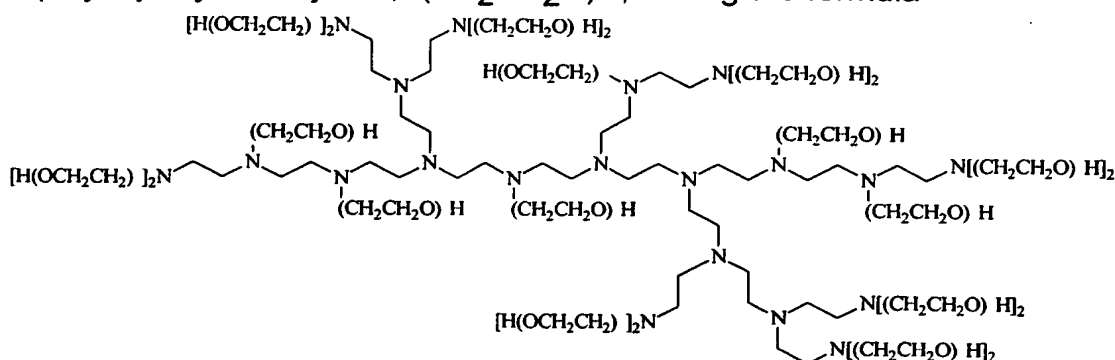
wherein R', m and n are the same as defined herein above. Preferred PEI's will have a molecular weight greater than 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Examples of amino-functional polymers comprising PEI's, are illustrated in Formulas I - IV:

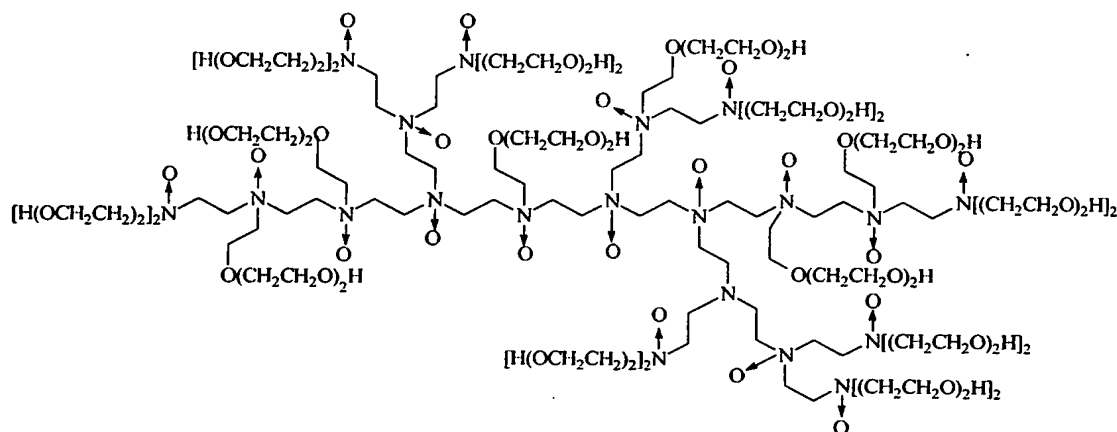
Formula I depicts an amino-functional polymer comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(\text{CH}_2\text{CH}_2\text{O})\text{H}$, having the formula



Formula I

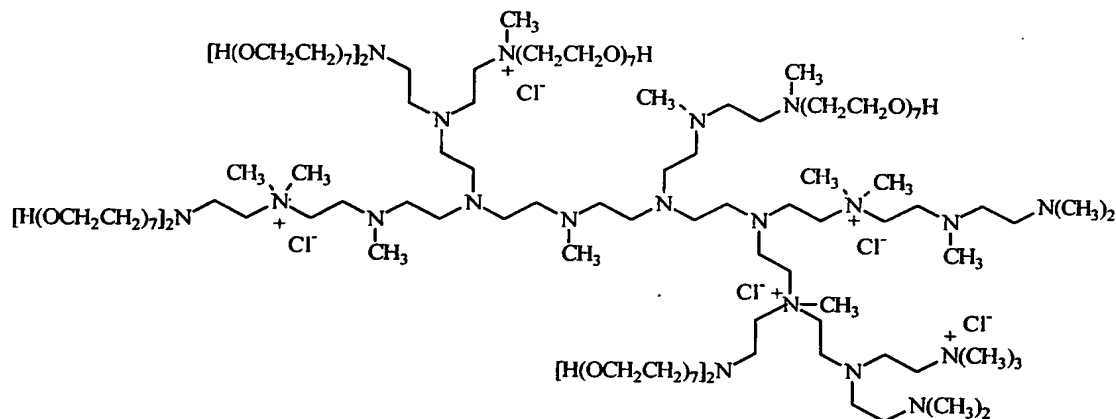
This is an example of an amino-functional polymer that is fully modified by one type of moiety.

Formula II depicts an amino-functional polymer comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(\text{CH}_2\text{CH}_2\text{O})_2\text{H}$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, said polymer having the formula



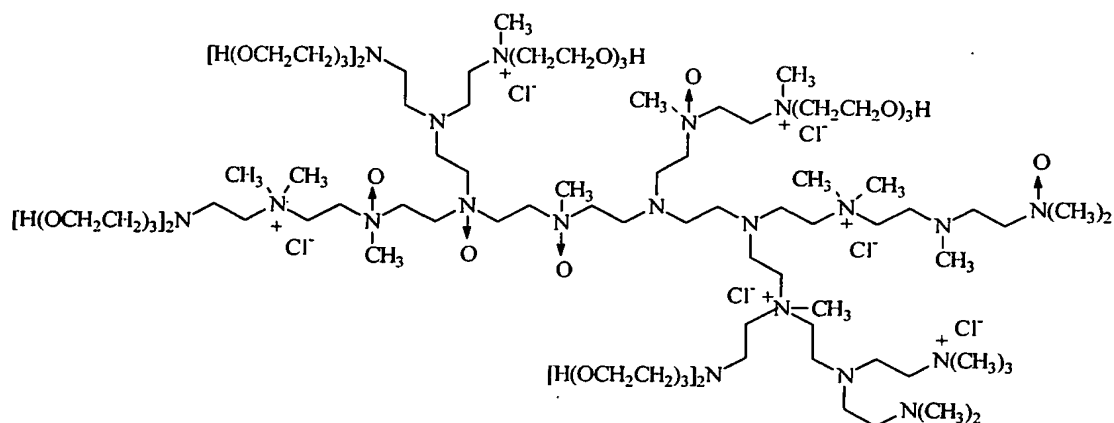
Formula II

- Formula III depicts an amino-functional polymer comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, or methyl groups. The modified PEI has the formula



Formula III

- Formula IV depicts an amino-functional polymer comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting polymer has the formula



Formula IV

In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of R' groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

Commercially available amino-functional polymers suitable for use herein are poly(ethyleneimine) with a MW 1200, hydroxyethylated poly(ethyleneimine) from Polysciences, with a MW 2000, and 80% hydroxyethylated poly(ethyleneimine) from Aldrich.

A typical amount of amino-functional polymer to be employed in the composition of the invention when used as sole nitrogen containing compound is of greater than 1%, preferably up to 50% by weight, more preferably from greater than 1% to 25% by weight, and most preferably from greater than 1% to 10% active by weight of the composition.

Dye fixing agent

Dye fixing agents, or "fixatives", are well-known, commercially available materials which are designed to improve the appearance of dyed fabrics by minimizing the loss of dye from fabrics due to washing. Not included within this definition are

components which are fabric softeners or those described hereinafter as amino-functional polymers.

Many dye fixing agents are cationic, and are based on various quaternized or otherwise cationically charged organic nitrogen compounds. Cationic fixatives are available under various trade names from several suppliers. Representative examples include: Cartafix CB from Clariant, CROSCOLOR PMF (July 1981, Code No. 7894) and CROSCOLOR NOFF (January 1988, Code No. 8544) from Crosfield; INDOSOL E-50 (February 27, 1984, Ref. No. 6008.35.84; polyethyleneamine-based) from Sandoz; SANDOFIX TPS, which is also available from Sandoz and is a preferred polycationic fixative for use herein and SANDOFIX SWE (cationic resinous compound), REWIN SRF, REWIN SRF-O and REWIN DWR from CHT-Beitlich GMBH, Tinofix® ECO, Tinofix® FRD and Solfin® available from Ciba-Geigy.

Other cationic dye fixing agents are described in "Aftertreatments for improving the fastness of dyes on textile fibres" by Christopher C. Cook (REV. PROG. COLORATION Vol. 12, 1982). Dye fixing agents suitable for use in the present invention are ammonium compounds such as fatty acid - diamine condensates e.g. the hydrochloride, acetate, methosulphate and benzyl hydrochloride of oleyldiethyl aminoethylamide, oleylmethyl-diethylenediaminemethosulphate, monostearyl-ethylene diaminotrimethylammonium methosulphate and oxidized products of tertiary amines; derivatives of polymeric alkyldiamines, polyamine-cyanuric chloride condensates and aminated glycerol dichlorohydrins.

Preferred dye fixing agents are the cellulose reactive dye fixing agents.

By "cellulose reactive dye fixing agent", it is meant that the agent reacts with the cellulose fibers upon heat treatment. The agents suitable for use herein can be defined by the following test procedure, so called cellulose reactivity test measurement.

Cellulose reactivity test measurement

Two pieces of bleeding fabrics (e.g. 10 x 10 cm of knitted cotton dyed with Direct Red 80) are soaked for 20 minutes in an aqueous solution of 1% (w/w) of the

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cellulose reactive dye fixing agent candidate. The pH of the solution is as it is obtained at this concentration.

5 The swatches are then dried. One of the dried swatches as well as an unsoaked swatch (control 1) are passed 10 times through an ironing calender set on a linen setting.

10 A control 2 swatch is also used in this measurement test which is a non-soaked and non-ironed swatch.

15 The 4 swatches are washed separately in Launder-o-meter pots under typical conditions with a commercial detergent used at the recommended dosage for ½ hour at 60°C, followed by a thorough rinsing of 4 times 200 ml of cold water and then line dried.

20 The wash-fastness is then measured on the swatches by determination of their so-called delta-E values versus a new, untreated swatch. Delta E's are defined, for instance, in ASTM D2244. Delta E is the computed color difference as defined in ASTM D2244, i.e the magnitude and direction of the difference between two psychophysical color stimuli defined by tristimulus values, or by chromaticity coordinates and luminance factor, as computed by means of a specified set of color-difference equations defined in the CIE 1976 CIELAB opponent-color space, the Hunter opponent-color space, the Friele-Mac Adam-Chickering color space or any equivalent color space.

25 Accordingly, the lower the Delta E versus new, the better the wash fastness improvement.

30 If the washfastness improvement of the ironed-soaked swatch is better than that of the non-ironed soak swatch and also better than the two respective control 1 and 2, then the candidate is a cellulose reactive dye fixing agent for the purpose of the invention.

35 Typical cellulose reactive dye fixing agents are products containing the reactive group of the reactive dye classes selected from halogeno-triazine products, vinyl sulphones compounds, epichlorhydrine derivatives, hydroxyethylene urea

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derivatives, formaldehyde condensation products, polycarboxylates, glyoxal and glutaraldehyde derivatives and mixtures thereof.

5 Other reactive functionalities for cellulose can be found in Textile processing and properties. Elsevier (1997) from Tyrone L. Vigo at page 120 to 121, which provides the use of specific electrophilic groups with cellulose affinity.

10 Preferred hydroxyethylene urea derivatives include dimethyloldihydroxyethylene, urea, and dimethyl urea glyoxal.

15 Preferred formaldehyde condensation products include the condensation products derived from formaldehyde and a group selected from an amino-group, an imino-group, a phenol group, an urea group, a cyanamide group and an aromatic group. Commercially available compounds among this class are Sandox WE 56 from Clariant, Zetex E from Zeneca and Levogen BF from Bayer.

20 Preferred polycarboxylates derivatives include butane tetracarboxylic acid derivatives, citric acid derivatives, polyacrylates and derivatives thereof.

25 A most preferred cellulosic reactive dye fixing agents is one of the hydroxyethylene urea derivatives class commercialised under the tradename of Indosol CR from Clariant. Still other most preferred cellulosic reactive dye fixing agents are commercialised under the tradename Rewin DWR and Rewin WBS from CHT R. Beitlich.

Among the dye fixing agents disclosed, the preferred agent for use in the present invention are cationic, in particular polycationic dye fixing agents.

30 A typical amount of the dye fixing agent to be employed in the composition of the invention is preferably from 1% to 50% by weight, more preferably from 1% to 25% by weight, most preferably from 1.5% to 10% active by weight of the composition.

35 When both the dye fixing agent and the polyamino-functional polymer are employed, the total level of these components is typically up to 90% by weight,

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preferably up to 50% by weight, more preferably from 1% to 25% by weight, most preferably from 1% to 10% active by weight of the composition.

Water-soluble cationic surface active agent

- 5 By "water-soluble wetting agent", it is meant that the wetting agent forms substantially clear, isotropic solutions when dissolved in water at 0.2 weight percent at 25°C.

- 10 Any type of water-soluble cationic surface active agent can be used to impart the scum reducing property. However, some water-soluble cationic surface active agents and mixtures thereof are more preferred. Hence, it is preferred that the cationic surfactant is a surface-active molecule with a linear or branched hydrophobic tail and a positively charged hydrophilic head group, more preferably, the cationic surfactant for use in the present invention is quaternary ammonium salt of formula:



- 20 wherein the R¹ group is C₁₀-C₂₂ hydrocarbon group, preferably C₁₂-C₁₈ alkyl group or the corresponding ester linkage interrupted group with a short alkylene (C₁-C₄) group between the ester linkage and the N, and having a similar hydrocarbon group, e.g., a fatty acid ester of choline, preferably C₁₂-C₁₄ (coco) choline ester and/or C₁₆-C₁₈ tallow choline ester. The hydrocarbon group may be interrupted by further groups like COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and
- 25 NHCOO. Each R is a C₁-C₄ alkyl or substituted (e.g., hydroxy) alkyl, or hydrogen, preferably methyl, and the counterion X⁻ is a softener compatible anion, for example, chloride, bromide, methyl surface, etc.

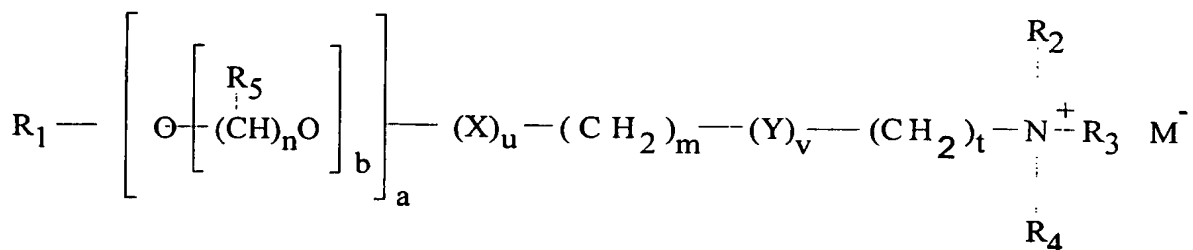
- 30 The long chain group R₁, of the single-long-chain-alkyl surfactant, typically contains an alkylene group having from 10 to 22 carbon atoms, preferably from 12 to about 16 carbon atoms, more preferably from 12 to 18 carbon atoms. This R₁ group can be attached to the cationic nitrogen atom through a group containing one, or more, ester, amide, ether, amine, etc., preferably ester, linking groups which can be desirable for increased hydrophilicity, biodegradability, etc.
- 35 Such linking groups are preferably within about three carbon atoms of the

nitrogen atom. A preferred cationic surfactant of this type is N,N dimethyl-N-(2-hydroxyethyl)-N-dodecyl/tetradecyl ammonium bromide.

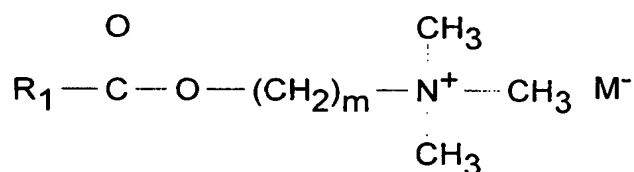
- 5 If the corresponding, non-quaternary amines are used, any acid (preferably a mineral or polycarboxylic acid) which is added to keep the ester groups stable will also keep the amine protonated in the compositions.

Typical disclosure of these cationic surfactants suitable for use in the present invention are the choline ester surfactants of formula:

10



- wherein R₁ is a C₁₀-C₂₂ linear or branched alkyl, alkenyl or alkaryl chain or M⁻. N⁺(R₆R₇R₈)(CH₂)_s; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R₂, R₃, R₄, R₆, R₇, and R₈ are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl and hydroxy-alkenyl groups having from 1 to 4 carbon atoms and alkaryl groups; and R₅ is independently H or a C₁-C₃ alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion.
- 25 Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide. Highly preferred water soluble choline ester surfactants are the esters having the formula:



where m is from 1 to 4, preferably 2 or 3 and wherein R₁ is a C₁₁-C₁₉ linear or branched alkyl chain.

5

Particularly preferred choline esters of this type include the stearoyl choline ester quaternary methylammonium halides (R¹=C₁₇ alkyl), palmitoyl choline ester quaternary methylammonium halides (R¹=C₁₅ alkyl), myristoyl choline ester quaternary methylammonium halides (R¹=C₁₃ alkyl), lauroyl choline ester methylammonium halides (R¹=C₁₁ alkyl), cocoyl choline ester quaternary methylammonium halides (R¹=C₁₁-C₁₃ alkyl), tallowyl choline ester quaternary methylammonium halides (R¹=C₁₅-C₁₇ alkyl), and any mixtures thereof.

10

Most particularly preferred choline esters of this type are selected from myristoyl choline ester quaternary methylammonium halides, lauroyl choline ester methylammonium halides, cocoyl choline ester quaternary methylammonium halides, and any mixtures thereof.

15

The particularly preferred choline esters, given above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, preferably in the presence of a solvent such as ethanol, water, propylene glycol or preferably a fatty alcohol ethoxylate such as C₁₀-C₁₈ fatty alcohol ethoxylate having a degree of ethoxylation of from 3 to 50 ethoxy groups per mole forming the desired cationic material. They may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then quaternized with trimethylamine, forming the desired cationic material.

20

25

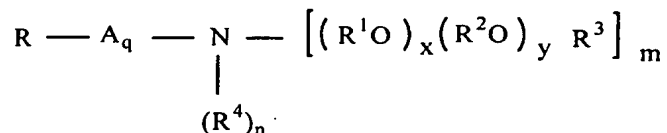
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Polyoxyalkylene alkyl amine surface active agent

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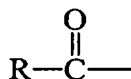
A polyoxyalkylene alkyl amine surface active agent is also another essential component of the present invention composition. Indeed, by means of this component, the formation of scum is reduced or even prevented.

- 5 Preferably, the polyoxyalkylene alkyl amine nonionic surfactants suitable for use in the present invention have the formula:



wherein R is selected from C₇-C₂₁ linear alkyl, C₇-C₂₁ branched alkyl, C₇-C₂₁ linear alkenyl, C₇-C₂₁ branched alkenyl, and mixtures thereof. The nonionic

- 10 surfactants of the present invention are derived from synthetic or naturally occurring feedstocks, preferably naturally occurring feedstock, therefore said nonionic surfactants comprise acyl units having the formula:



- 15 wherein said acyl unit is derived from a source of triglyceride selected from the group consisting of tallow, partially hydrogenated tallow, lard, coconut oil, partially hydrogenated coconut oil, palm kernel oil, hydrogenated palm kernel oil, canola oil, partially hydrogenated canola oil, safflower oil, partially hydrogenated safflower oil, peanut oil, partially hydrogenated peanut oil, sunflower oil, partially
20 hydrogenated sunflower oil, corn oil, partially hydrogenated corn oil, soybean oil, partially hydrogenated soybean oil, tall oil, partially hydrogenated tall oil, rice bran oil, partially hydrogenated rice bran oil, and mixtures thereof. Further preferred sources of triglyceride for the acyl unit are synthetic triglyceride feedstocks, for example, triglycerides which are prepared via chemical reaction or other process
25 rather than being derived from a natural source. More preferred feedstocks for said acyl units are tallow, partially hydrogenated tallow, coconut oil, partially hydrogenated coconut oil, canola oil, hydrogenated canola oil, synthetic triglycerides, and mixtures thereof. A preferred triglyceride source is tri-oleyl triglycerides.

30

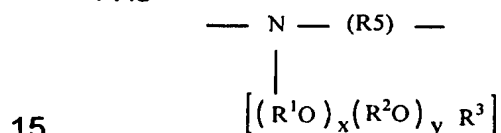
R¹ is ethylene; R² is selected from C₃-C₄ linear alkyl, C₃-C₄ branched alkyl, and mixtures thereof; preferably R² is 1,2-propylene. Nonionic surfactants which comprise a mixture of R¹ and R² units preferably comprise from about 4 to about 12

ethylene units in combination with from about 1 to about 4 1,2-propylene units. The units may be alternating, or grouped together in any combination suitable to the formulator. Preferably the ratio of R¹ units to R² units is from about 4 : 1 to about 8 : 1. Preferably an R² units (i.e. 1,2-propylene) is attached to the nitrogen atom
5 followed by the balance of the chain comprising from 4 to 8 ethylene units.

R³ is selected from hydrogen, C₁-C₄ linear alkyl, C₃-C₄ branched alkyl, and mixtures thereof; preferably hydrogen or methyl, more preferably hydrogen.

10 R⁴ is selected from hydrogen, C₁-C₄ linear alkyl, C₃-C₄ branched alkyl, and mixtures thereof; preferably hydrogen. When the index m is equal to 2 the index n must be equal to 0 and the R⁴ unit is absent and is instead replaced by a - [(R¹O)_x(R²O)_yR³] unit.

A is



R⁵ is selected from -[(R¹O)_x(R²O)_y] unit, C₁-C₁₆ linear alkyl, C₁-C₁₆ branched alkyl, C₁-C₁₆ linear alkenyl, C₁-C₁₆ branched alkenyl, and mixtures thereof,
20 preferably is selected from a C₃ linear alkyl, C₃ branched alkyl, C₃ linear alkenyl, C₃ branched alkenyl, and mixtures thereof.

The index m is 1 or 2, the index n is 0 or 1, provided that when m is equal to 1, n is equal to 1; and when m is 2 n is 0; preferably m is equal to 2 and n is equal to 0,
25 resulting in two -[(R¹O)_x(R²O)_yR³] unit and R⁴ being absent. The index x is from 0 to about 50, preferably from about 1 to about 25, more preferably from about 3 to about 10. The index y is from 0 to about 10, preferably 0, however when the index y is not equal to 0, y is from 1 to about 4. Preferably all of the alkyleneoxy units are ethyleneoxy units. Those skilled in the art of ethoxylated polyoxyalkylene
30 alkyl amine surface active agents will recognized that the values for the indices x and y are average values and the true values may range over several values depending upon the process used to alkoxylate the amines.

The index q is 0 or 1.

Polyoxyalkylene alkylamines are available under various trade names from several suppliers. Representative examples include: Ethomeen, Ethoduomeen from Akzo Chemicals, and/or Secomine from Stepan.

5

The polyoxyalkylene alkylamine surface active agents are typically present at levels of from 0.001% to 20% by weight, preferably from 0.5% to 12% by weight, more preferably from 1% to 8% by weight of the composition.

- 10 Preferred among the scum reducing agent herein described are the water-soluble cationic surface active agents.

- 15 To further improve the scum reduction performance of the composition, it has also been found preferred, when the polyamino-functional polymer as described above is the sole nitrogen containing compounds, that the scum reducing agent and the polymer are present in weight ratios of 0.02:1 to 2:1, preferably 0.05:1 to 1.5:1, most preferably from 0.1:1 to 0.8:1.

- 20 When the dye fixing agent is the sole nitrogen containing compounds, it has been found preferred to have, for optimum scum reduction, a weight ratio of scum reducing agent to dye fixing of 0.05:1 to 5:1, more preferably 0.1:1 to 2.5:1, most preferably from 0.5:1 to 1:1.

- 25 When mixture of polyamino-functional polymer and dye fixing agents are used, it is preferred to have, for improved scum reduction, a weight ratio of scum reducing agent to the sum of polyamino-functional polymer and dye fixing agents of from 0.05:1 to 2:1, preferably from 0.1:1 to 1:1.

- 30 In addition to the above described scum reducing agents, it has been found that the use of water-insoluble cationic surface active agent commonly known as fabric softening compound also provides beneficial reduction in the scum reduction performance.

Fabric softening compound

- 35 Typical levels of incorporation of the softening compound in the composition are of from 1% to 80% by weight, preferably from 5% to 75%, more preferably from

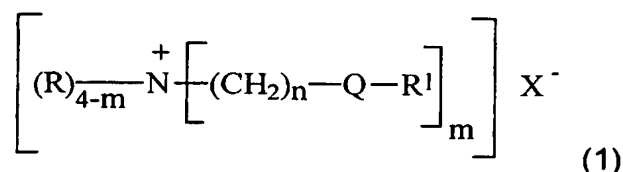
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15% to 70%, and even more preferably from 19% to 65%, by weight of the composition.

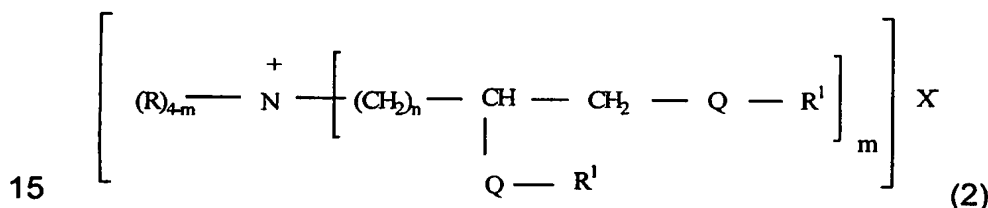
5 Typical of the cationic softening components are the quaternary ammonium compounds or amine precursors thereof as defined hereinafter.

A)-Quaternary Ammonium Fabric Softening Active Compound

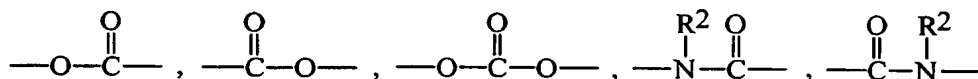
10 (1) Preferred quaternary ammonium fabric softening active compound have the formula



or the formula:

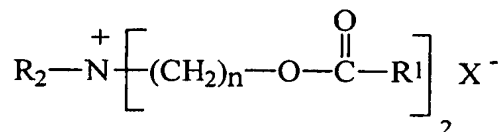


wherein Q is a carbonyl unit having the formula:



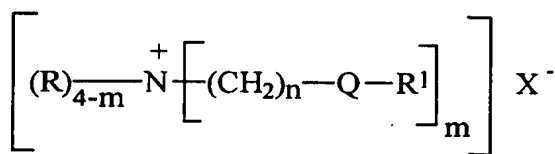
each R unit is independently hydrogen, C₁-C₆ alkyl, C₁-C₆ hydroxyalkyl, and
 20 mixtures thereof, preferably methyl or hydroxy alkyl; each R¹ unit is
 independently linear or branched C₁₁-C₂₂ alkyl, linear or branched C₁₁-C₂₂
 alkenyl, and mixtures thereof, R² is hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl,
 and mixtures thereof; X is an anion which is compatible with fabric softener
 25 actives and adjunct ingredients; the index m is from 1 to 4, preferably 2; the index
 n is from 1 to 4, preferably 2.

An example of a preferred fabric softener active is a mixture of quaternized amines having the formula:

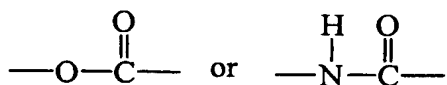


wherein R is preferably methyl; R¹ is a linear or branched alkyl or alkenyl chain comprising at least 11 atoms, preferably at least 15 atoms. In the above fabric softener example, the unit -O₂CR¹ represents a fatty acyl unit which is typically derived from a triglyceride source. The triglyceride source is preferably derived from tallow, partially hydrogenated tallow, lard, partially hydrogenated lard, vegetable oils and/or partially hydrogenated vegetable oils, such as, canola oil, safflower oil, peanut oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil, etc. and mixtures of these oils.

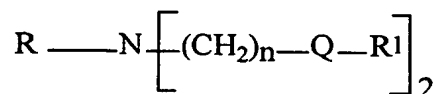
The preferred fabric softening actives of the present invention are the Diester and/or Diamide Quaternary Ammonium (DEQA) compounds, the diesters and diamides having the formula:



wherein R, R¹, X, and n are the same as defined herein above for formulas (1) and (2), and Q has the formula:

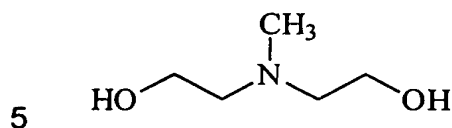


These preferred fabric softening actives are formed from the reaction of an amine with a fatty acyl unit to form an amine intermediate having the formula:

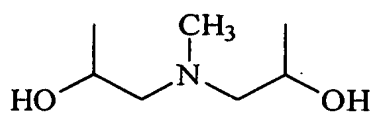


wherein R is preferably methyl, Q and R¹ are as defined herein before; followed by quaternization to the final softener active.

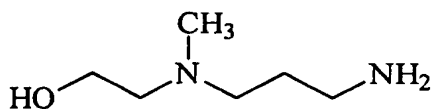
Non-limiting examples of preferred amines which are used to form the DEQA fabric softening actives according to the present invention include methyl bis(2-hydroxyethyl)amine having the formula:



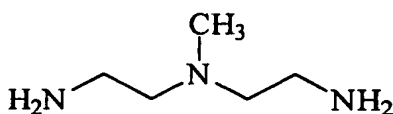
methyl bis(2-hydroxypropyl)amine having the formula:



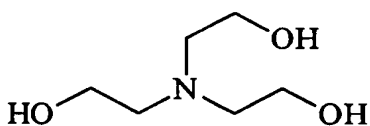
methyl (3-aminopropyl) (2-hydroxyethyl)amine having the formula:



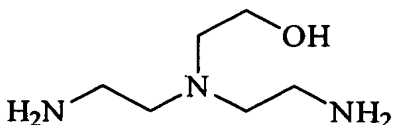
methyl bis(2-aminoethyl)amine having the formula:



triethanol amine having the formula:



di(2-aminoethyl) ethanolamine having the formula:



The counterion, $X^{(-)}$ above, can be any softener-compatible anion, preferably the anion of a strong acid, for example, chloride, bromide, methylsulfate, ethylsulfate, sulfate, nitrate and the like, more preferably chloride or methyl

sulfate. The anion can also, but less preferably, carry a double charge in which case $X^{(-)}$ represents half a group.

- 5 Tallow and canola oil are convenient and inexpensive sources of fatty acyl units which are suitable for use in the present invention as R^1 units. The following are non-limiting examples of quaternary ammonium compounds suitable for use in the compositions of the present invention. The term "tallowyl" as used herein below indicates the R^1 unit is derived from a tallow triglyceride source and is a mixture of fatty acyl units. Likewise, the use of the term canolyl refers to a mixture of fatty acyl units derived from canola oil.
- 10

Table II

Fabric Softener Actives

- 15 N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(canolyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
N,N-di(canolyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium chloride;
N,N-di(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-canolyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride
- 20 N,N-di(2-tallowyloxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
N,N-di(2-canolyl-oxyethylcarbonyloxyethyl)-N,N-dimethyl ammonium chloride;
N-(2-tallowyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
N-(2-canolyl-oxy-2-ethyl)-N-(2-canolyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 25 N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
N,N,N-tricanolyl-oxy-ethyl)-N-methyl ammonium chloride;
N-(2-tallowyloxy-2-oxoethyl)-N-(tallowyl)-N,N-dimethyl ammonium chloride;
N-(2-canolyl-oxy-2-oxoethyl)-N-(canolyl)-N,N-dimethyl ammonium chloride;
- 30 1,2-ditallowyloxy-3-N,N,N-trimethylammoniopropane chloride; and
1,2-dicanolyl-oxy-3-N,N,N-trimethylammoniopropane chloride;
and mixtures of the above actives.

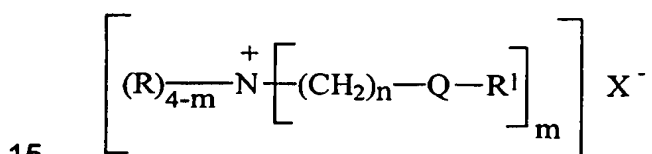
- 35 Other examples of quaternary ammonium softening compounds are methylbis(tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium

methylsulfate; these materials are available from Witco Chemical Company under the trade names Varisoft® 222 and Varisoft® 110, respectively.

5 Particularly preferred is N,N-di(tallowoyl-oxy-ethyl)-N,N-dimethyl ammonium chloride, where the tallow chains are at least partially unsaturated.

10 The level of unsaturation contained within the tallow, canola, or other fatty acyl unit chain can be measured by the Iodine Value (IV) of the corresponding fatty acid, which in the present case should preferably be in the range of from 5 to 100 with two categories of compounds being distinguished, having a IV below or above 25.

Indeed, for compounds having the formula:



derived from tallow fatty acids, when the Iodine Value is from 5 to 25, preferably 15 to 20, it has been found that a *cis/trans* isomer weight ratio greater than about 30/70, preferably greater than about 50/50 and more preferably greater than about 70/30 provides optimal concentrability.

20 For compounds of this type made from tallow fatty acids having a Iodine Value of above 25, the ratio of *cis* to *trans* isomers has been found to be less critical unless very high concentrations are needed.

Other suitable examples of fabric softener actives are derived from fatty acyl groups wherein the terms "tallowyl" and "canolyl" in the above examples are
25 replaced by the terms "cocoyl, palmoyl, lauryl, oleyl, ricinoleyl, stearyl, palmityl," which correspond to the triglyceride source from which the fatty acyl units are derived. These alternative fatty acyl sources can comprise either fully saturated, or preferably at least partly unsaturated chains.

30 As described herein before, R units are preferably methyl, however, suitable fabric softener actives are described by replacing the term "methyl" in the above examples in Table II with the units "ethyl, ethoxy, propyl, propoxy, isopropyl, butyl, isobutyl and t-butyl.

The counter ion, X, in the examples of Table II can be suitably replaced by bromide, methylsulfate, formate, sulfate, nitrate, and mixtures thereof. In fact, the anion, X, is merely present as a counterion of the positively charged quaternary ammonium compounds. The scope of this invention is not considered limited to any particular anion.

For the preceding ester fabric softening agents, the pH of the compositions herein is an important parameter of the present invention. Indeed, it influences the stability of the quaternary ammonium or amine precursors compounds, especially in prolonged storage conditions.

The pH, as defined in the present context, is measured in the neat compositions at 20 °C. While these compositions are operable at pH of less than about 6.0, for optimum hydrolytic stability of these compositions, the neat pH, measured in the above-mentioned conditions, must preferably be in the range of from about 2.0 to about 5, preferably in the range of 2.5 to 4.5, preferably about 2.5 to about 3.5. The pH of these compositions herein can be regulated by the addition of a Bronsted acid.

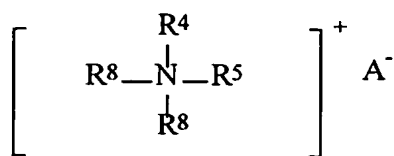
Examples of suitable acids include the inorganic mineral acids, carboxylic acids, in particular the low molecular weight (C₁-C₅) carboxylic acids, and alkylsulfonic acids. Suitable inorganic acids include HCl, H₂SO₄, HNO₃ and H₃PO₄. Suitable organic acids include formic, acetic, citric, methylsulfonic and ethylsulfonic acid. Preferred acids are citric, hydrochloric, phosphoric, formic, methylsulfonic acid, and benzoic acids.

As used herein, when the diester is specified, it will include the monoester that is normally present in manufacture. For softening, under no/low detergent carry-over laundry conditions the percentage of monoester should be as low as possible, preferably no more than about 2.5%. However, under high detergent carry-over conditions, some monoester is preferred. The overall ratios of diester to monoester are from about 100:1 to about 2:1, preferably from about 50:1 to about 5:1, more preferably from about 13:1 to about 8:1. Under high detergent carry-over conditions, the di/monoester ratio is preferably about 11:1. The level of monoester present can be controlled in the manufacturing of the softener compound.

Mixtures of actives of formula (1) and (2) may also be prepared.

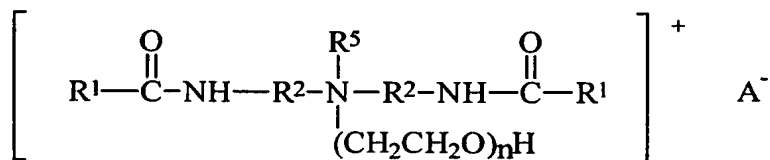
- 2)-Still other suitable quaternary ammonium fabric softening compounds for use herein are cationic nitrogenous salts having two or more long chain acyclic aliphatic C₈-C₂₂ hydrocarbon groups or one said group and an arylalkyl group which can be used either alone or as part of a mixture are selected from the group consisting of:

(i) acyclic quaternary ammonium salts having the formula:



wherein R⁴ is an acyclic aliphatic C₈-C₂₂ hydrocarbon group, R⁵ is a C₁-C₄ saturated alkyl or hydroxyalkyl group, R⁸ is selected from the group consisting of R⁴ and R⁵ groups, and A⁻ is an anion defined as above;

(ii) diamino alkoxyated quaternary ammonium salts having the formula:



- wherein n is equal to 1 to about 5, and R¹, R², R⁵ and A⁻ are as defined above;
(iii) mixtures thereof.

Examples of the above class cationic nitrogenous salts are the well-known dialkyldi methylammonium salts such as ditallowdimethylammonium chloride, ditallowdimethylammonium methylsulfate, di(hydrogenatedtallow)dimethylammonium chloride, distearyldimethylammonium chloride, dibehenyldimethylammonium chloride. Di(hydrogenatedtallow)di methylammonium chloride and ditallowdimethylammonium chloride are preferred. Examples of commercially available dialkyldimethyl ammonium salts usable in the present invention are di(hydrogenatedtallow)dimethylammonium chloride (trade name Adogen® 442), ditallowdimethylammonium chloride (trade name

Adogen® 470, Praepagen® 3445), distearyl dimethylammonium chloride (trade name Arosurf® TA-100), all available from Witco Chemical Company. Dibehenyl dimethylammonium chloride is sold under the trade name Kemamine Q-2802C by Humko Chemical Division of Witco Chemical Corporation.

- 5 Dimethylstearylbenzyl ammonium chloride is sold under the trade names Varisoft® SDC by Witco Chemical Company and Ammonyx® 490 by Onyx Chemical Company.

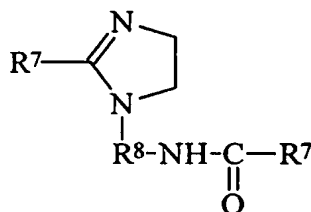
B)-Amine Fabric Softening Active Compound

- 10 Suitable amine fabric softening compounds for use herein, which may be in amine form or cationic form are selected from:

- (i)- Reaction products of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof. These reaction products are mixtures of several compounds in view of the multi-functional structure of the polyamines.

The preferred Component (i) is a nitrogenous compound selected from the group consisting of the reaction product mixtures or some selected components of the mixtures.

- 20 One preferred component (i) is a compound selected from the group consisting of substituted imidazoline compounds having the formula:



- 25 wherein R⁷ is an acyclic aliphatic C₁₅-C₂₁ hydrocarbon group and R⁸ is a divalent C₁-C₃ alkylene group.

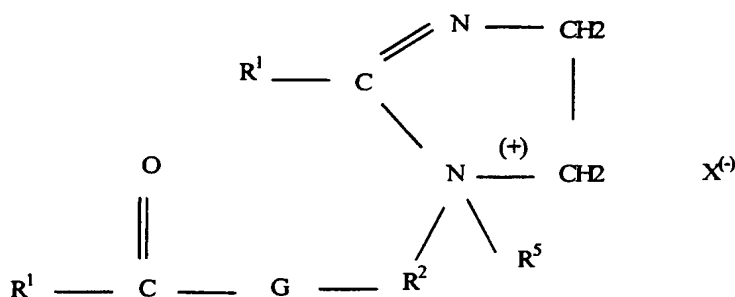
- Component (i) materials are commercially available as: Mazamide® 6, sold by Mazer Chemicals, or Ceranine® HC, sold by Sandoz Colors & Chemicals; stearic hydroxyethyl imidazoline sold under the trade names of Alkazine® ST by Alkaril Chemicals, Inc., or Schercozoline® S by Scher Chemicals, Inc.; N,N'-ditallowalkoyldiethylenetriamine; 1-tallowamidoethyl-2-tallowimidazoline (wherein

in the preceding structure R¹ is an aliphatic C₁₅-C₁₇ hydrocarbon group and R⁸ is a divalent ethylene group).

5 Certain of the Components (i) can also be first dispersed in a Bronsted acid dispersing aid having a pKa value of not greater than about 4; provided that the pH of the final composition is not greater than about 6. Some preferred dispersing aids are hydrochloric acid, phosphoric acid, or methylsulfonic acid.

Both N,N"-ditallowalkoyldiethylenetriamine and 1-tallow(amidoethyl)-2-tallowimidazoline are reaction products of tallow fatty acids and diethylenetriamine, and are precursors of the cationic fabric softening agent methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate (see "Cationic Surface Active Agents as Fabric Softeners," R. R. Egan, Journal of the American Oil Chemicals' Society, January 1978, pages 118-121). N,N"-ditallow alkoyldiethylenetriamine and 1-tallowamidoethyl-2-tallowimidazoline can be obtained from Witco Chemical Company as experimental chemicals. Methyl-1-tallowamidoethyl-2-tallowimidazolinium methylsulfate is sold by Witco Chemical Company under the tradename Varisoft® 475.

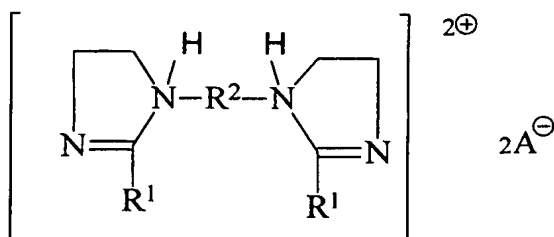
20 (ii)-softener having the formula:



wherein each R² is a C₁₋₆ alkylene group, preferably an ethylene group; and G
25 is an oxygen atom or an -NR- group; and each R, R¹, R² and R⁵ have the
definitions given above and A⁻ has the definitions given above for X⁻.

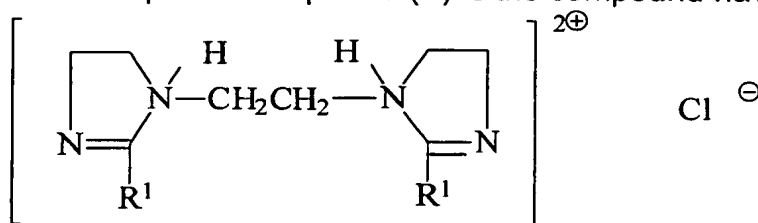
An example of Compound (ii) is 1-oleylamidoethyl-2-oleylimidazolium chloride wherein R¹ is an acyclic aliphatic C₁₅-C₁₇ hydrocarbon group, R² is an ethylene group, G is a NH group, R⁵ is a methyl group and A⁻ is a chloride anion.

30 (iii)- softener having the formula:



wherein R, R¹, R², and A⁻ are defined as above.

- 5 An example of Compound (iii) is the compound having the formula:



wherein R¹ is derived from oleic acid.

- Additional fabric softening agents useful herein are described in U.S. Pat. No. 4,661,269, issued April 28, 1987, in the names of Toan Trinh, Errol H. Wahl, Donald M. Swartley, and Ronald L. Hemingway; U.S. Pat. No. 4,439,335, Burns, issued March 27, 1984; and in U.S. Pat. Nos.: 3,861,870, Edwards and Diehl; 4,308,151, Cambre; 3,886,075, Bernardino; 4,233,164, Davis; 4,401,578, Verbruggen; 3,974,076, Wiersema and Rieke; 4,237,016, Rudkin, Clint, and Young; and European Patent Application publication No. 472,178, by Yamamura et al., all of said documents being incorporated herein by reference.

Of course, the term "softening active" can also encompass mixed softening active agents.

- 20 Preferred among the classes of softener compounds disclosed herein before are the diester or diamido quaternary ammonium fabric softening active compound (DEQA).

- 25 Fully formulated fabric care compositions may contain, in addition to the hereinbefore described components, one or more of the following ingredients.

OPTIONAL INGREDIENTS

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(A)Liquid carrier

Another optional, but preferred, ingredient is a liquid carrier. The liquid carrier employed in the instant compositions is preferably at least primarily water due to its low cost, relative availability, safety, and environmental compatibility. The level of water in the liquid carrier is preferably at least about 50%, most preferably at least about 60%, by weight of the carrier. Mixtures of water and low molecular weight, e.g., <about 200, organic solvent, e.g., lower alcohols such as ethanol, propanol, isopropanol or butanol are useful as the carrier liquid. Low molecular weight alcohols include monohydric, dihydric (glycol, etc.) trihydric (glycerol, etc.), and higher polyhydric (polyols) alcohols.

(B)-Additional Solvents

The compositions of the present invention may comprise one or more solvents which provide increased ease of formulation. These ease of formulation solvents are all disclosed in WO 97/03169. This is particularly the case when formulating liquid, clear fabric softening compositions. When employed, the ease of formulation solvent system preferably comprises less than about 40%, preferably from about 10% to about 35%, more preferably from about 12% to about 25%, and even more preferably from about 14% to about 20%, by weight of the composition. The ease of formulation solvent is selected to minimize solvent odor impact in the composition and to provide a low viscosity to the final composition. For example, isopropyl alcohol is not very effective and has a strong odor. n-Propyl alcohol is more effective, but also has a distinct odor. Several butyl alcohols also have odors but can be used for effective clarity/stability, especially when used as part of a ease of formulation solvent system to minimize their odor. The alcohols are also selected for optimum low temperature stability, that is they are able to form compositions that are liquid with acceptable low viscosities and translucent, preferably clear, down to about 40°F (about 4.4°C) and are able to recover after storage down to about 20°F (about 6.7°C).

The suitability of any ease of formulation solvent for the formulation of the liquid, concentrated, preferably clear, fabric softener compositions herein with the requisite stability is surprisingly selective. Suitable solvents can be selected based upon their octanol/water partition coefficient (P) as defined in WO 97/03169.

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The ease of formulation solvents herein are selected from those having a ClogP of from about 0.15 to about 0.64, preferably from about 0.25 to about 0.62, and more preferably from about 0.40 to about 0.60, said ease of formulation solvent preferably being at least somewhat asymmetric, and preferably having a melting, or solidification, point that allows it to be liquid at, or near room temperature. Solvents that have a low molecular weight and are biodegradable are also desirable for some purposes. The more assymmetric solvents appear to be very desirable, whereas the highly symmetrical solvents such as 1,7-heptanediol, or 1,4-bis(hydroxymethyl) cyclohexane, which have a center of symmetry, appear to be unable to provide the essential clear compositions when used alone, even though their ClogP values fall in the preferred range.

The most preferred ease of formulation solvents can be identified by the appearance of the softener vesicles, as observed via cryogenic electron microscopy of the compositions that have been diluted to the concentration used in the rinse. These dilute compositions appear to have dispersions of fabric softener that exhibit a more unilamellar appearance than conventional fabric softener compositions. The closer to uni-lamellar the appearance, the better the compositions seem to perform. These compositions provide surprisingly good fabric softening as compared to similar compositions prepared in the conventional way with the same fabric softener active.

Operable ease of formulation solvents are disclosed and listed below which have ClogP values which fall within the requisite range. These include mono-ols, C6 diols, C7 diols, octanediol isomers, butanediol derivatives, trimethylpentanediol isomers, ethylmethylpentanediol isomers, propyl pentanediol isomers, dimethylhexanediol isomers, ethylhexanediol isomers, methylheptanediol isomers, octanediol isomers, nonanediol isomers, alkyl glyceryl ethers, di(hydroxy alkyl) ethers, and aryl glyceryl ethers, aromatic glyceryl ethers, alicyclic diols and derivatives, C₃C₇ diol alkoxylated derivatives, aromatic diols, and unsaturated diols. Particularly preferred ease of formulation solvents include hexanediols such as 1,2-Hexanediol and 2-Ethyl-1,3-hexanediol and pentanediols such as 2,2,4-Trimethyl-1,3-pentanediol.

(C) Dispersibility Aids

Relatively concentrated compositions containing both saturated and unsaturated diester quaternary ammonium compounds can be prepared that are stable without the addition of concentration aids. However, the compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. These concentration aids which typically can be viscosity modifiers may be needed, or preferred, for ensuring stability under extreme conditions when particular softener active levels are used. The surfactant concentration aids are typically selected from the group consisting of (1) single long chain alkyl cationic surfactants; (2) nonionic surfactants; (3) amine oxides; (4) fatty acids; and (5) mixtures thereof. These aids are described in WO 94/20597, specifically on page 14, line 12 to page 20, line 12, which is herein incorporated by reference.

When said dispersibility aids are present, the total level is from 2% to 25%, preferably from 3% to 17%, more preferably from 4% to 15%, and even more preferably from 5% to 13% by weight of the composition. These materials can either be added as part of the active softener raw material, (I), e.g., the fatty acid which are reactants used to form the biodegradable fabric softener active as discussed hereinbefore, or added as a separate component. The total level of dispersibility aid includes any amount that may be present as part of component (I).

Inorganic viscosity/dispersibility control agents which can also act like or augment the effect of the surfactant concentration aids, include water-soluble, ionizable salts which can also optionally be incorporated into the compositions of the present invention. A wide variety of ionizable salts can be used. Examples of suitable salts are the halides of the Group IA and IIA metals of the Periodic Table of the Elements, e.g., calcium chloride, magnesium chloride, sodium chloride, potassium bromide, and lithium chloride. The ionizable salts are particularly useful during the process of mixing the ingredients to make the compositions herein, and later to obtain the desired viscosity. The amount of ionizable salts used depends on the amount of active ingredients used in the compositions and can be adjusted according to the desires of the formulator. Typical levels of salts used to control the composition viscosity are from about 20 to about 20,000 parts per million (ppm), preferably from about 20 to about 11,000 ppm, by weight of the composition.

Alkylene polyammonium salts can be incorporated into the composition to give viscosity control in addition to or in place of the water-soluble, ionizable salts above. In addition, these agents can act as scavengers, forming ion pairs with anionic detergent carried over from the main wash, in the rinse, and on the fabrics, and may improve softness performance. These agents may stabilize the viscosity over a broader range of temperature, especially at low temperatures, compared to the inorganic electrolytes.

Specific examples of alkylene polyammonium salts include L-lysine monohydrochloride and 1,5-diammonium 2-methyl pentane dihydrochloride.

(D)-Stabilizers

Stabilizers can be present in the compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%, more preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions for the compositions and compounds stored in molten form. The use of antioxidants and reductive agent stabilizers is especially critical for low scent products (low perfume).

Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C8-C22) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171; Irganox® 1425; Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof; more preferably Irganox® 3125 alone or mixed with citric acid and/or other chelators such as isopropyl citrate, Dequest® 2010, available from

Monsanto with a chemical name of 1-hydroxyethylidene-1, 1-diphosphonic acid (etidronic acid), and Tiron®, available from Kodak with a chemical name of 4,5-dihydroxy-m-benzene-sulfonic acid/sodium salt, EDDS, and DTPA®, available from Aldrich with a chemical name of diethylenetriaminepentaacetic acid. The chemical names and CAS numbers for some of the above stabilizers are listed in Table II below.

TABLE II

	Antioxidant	CAS No.	Chemical Name used in Code of Federal
			Regulations
10	Irganox® 1010	6683-19-8	Tetrakis (methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)) methane
	Irganox® 1035	41484-35-9	Thiodiethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamate
	Irganox® 1098	23128-74-7	N,N'-Hexamethylene bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamamide
15	Irganox® B 1171	31570-04-4	
		23128-74-7	1:1 Blend of Irganox® 1098 and Irgafos® 168
	Irganox® 1425	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)
20	Irganox® 3114	65140-91-2	Calcium bis(monoethyl(3,5-di-tert-butyl-4-hydroxybenzyl)phosphonate)
	Irganox® 3125	34137-09-2	3,5-Di-tert-butyl-4-hydroxy-hydrocinnamic acid triester with 1,3,5-tris(2-hydroxyethyl)-S-triazine-2,4,6-(1H, 3H, 5H)-trione
25	Irgafos® 168	31570-04-4	Tris(2,4-di-tert-butyl-phenyl)phosphite

Examples of reductive agents include sodium borohydride, hypophosphorous acid, Irgafos® 168, and mixtures thereof.

30 (E)-Soil Release Agent

Soil Release agents are desirably used in fabric softening compositions of the instant invention. Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered

thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

5

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

10 The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, *et al.*, issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel *et al.*, issued November 6; U.S. 4,702,857, 15 Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado *et al.*, issued October 31, 1989; U.S. 4,956,447, Gosselink *et al.*, issued September 11, 1990; U.S. 5,415,807 Gosselink *et al.*, issued May 16, 1995; European Patent Application 0 219 048, published April 20 22, 1987 by Kud, *et al.*.

Further suitable soil release agents are described in U.S. 4,201,824, Violland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681, Ruppert *et al.*; U.S. 4,240,918; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 25 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN 30 type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

(F)-Bactericides

35 Examples of bactericides used in the compositions of this invention include glutaraldehyde, formaldehyde, 2-bromo-2-nitro-propane-1,3-diol sold by Inolex Chemicals, located in Philadelphia, Pennsylvania, under the trade name

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Bronopol[®], and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon 1 to 1,000 ppm by weight of the agent.

5 (G)-Perfume

The present invention can contain a perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

10 As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also
15 included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl
20 cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpeneol; 3,7-dimethyl-*cis*-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-*trans*-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecenyl
25 propionate; tricyclodecenyl acetate; anisaldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

30 Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methylether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate;
35 methylphenylcarbonyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-

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- cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecandioic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl;
- 5 methyl-1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanolide;
- 10 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate;
- 15 patchouli; olibanum resinoid; labdanum; vetivert; copaiba balsam; fir balsam; and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.
- More examples of perfume components are geraniol; geranyl acetate; linalool;
- 20 linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopyl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbinyl methylphenylcarbinyl acetate; isononyl acetate;
- 25 vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert-butylphenyl)-propanal; 2-methyl-3-(p-isopropylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentyl-cyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate;
- 30 phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methylether; isolongifolanone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionomes; irones; cis-3-hexenol and esters thereof; indane musk fragrances;
- 35 tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

5 Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

10 Perfume can be present at a level of from 0% to 10%, preferably from 0.1% to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

15 Perfume ingredients may also be suitably added as releasable fragrances, for example, as pro-perfumes or pro-fragrances as described in U.S. 5,652,205 Hartman et al., issued July 29, 1997 incorporated herein by reference.

20 (H)-Enzyme

The compositions and processes herein can optionally employ one or more enzymes such as lipases, proteases, cellulase, amylases and peroxidases. A preferred enzyme for use herein is a cellulase enzyme. Indeed, this type of enzyme will further provide a color care benefit to the treated fabric. Cellulases

25 usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307 discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*.

30 Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. Other suitable cellulases are also disclosed in WO 91/17243 to Novo, WO 96/34092, WO 96/34945 and EP-A-0,739,982. In practical terms for current commercial preparations, typical amounts are up to 5 mg by weight, more

35 typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise

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from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. In the particular cases where activity of the enzyme preparation can be defined otherwise such as with cellulases, corresponding activity units are preferred (e.g. CEVU or cellulase Equivalent Viscosity Units). For instance, the compositions of the present invention can contain cellulase enzymes at a level equivalent to an activity from 0.5 to 1000 CEVU/gram of composition. Cellulase enzyme preparations used for the purpose of formulating the compositions of this invention typically have an activity comprised between 1,000 and 10,000 CEVU/gram in liquid form, around 1,000 CEVU/gram in solid form.

(I)-Crystal growth inhibitor component

The compositions of the present invention can further contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, and/or organo monophosphonic acid, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the compositions.

By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

The organo diphosphonic acid is preferably a C₁-C₄ diphosphonic acid, more preferably a C₂ diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

Still useful herein as crystal growth inhibitor are the organic monophosphonic acid

Organo monophosphonic acid or one of its salts or complexes is also suitable for use herein as a CGI.

By organo monophosphonic acid it is meant herein an organo monophosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however

may be included in compositions of the invention as heavy metal ion sequestrants.

5 The organo monophosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred.

10 A preferred organo monophosphonic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer under the tradename of Bayhibit.

Other Optional Ingredients

15 The present invention can include optional components conventionally used in textile treatment compositions, for example: brighteners, colorants; surfactants; anti-shrinkage agents; fabric crisping agents; spotting agents; germicides; fungicides; anti-oxidants such as butylated hydroxy toluene, anti-corrosion agents, antifoam agents, and the like.

20 The present invention can also include other compatible ingredients, including those as disclosed in WO96/02625, WO96/21714, and WO96/21715, and dispersible polyolefin such as Velustrol® as disclosed in co-pending application PCT/US 97/01644, and the like. The present invention can also contain optional chelating agents such as ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in
25 the form of its sodium salt (EDDS) and crystal growth inhibitors such as glycolic acid and/or 1,1-hydroxyethane diphosphonic acid (HEDP).

Form of the composition

30 The fabric care composition can take a variety of physical forms including liquid such as aqueous or non-aqueous compositions and solid forms such as solid particulate forms.

Such compositions may be applied onto a substrate such as a dryer sheet product, used as a rinse added product, or as a spray or foam product.

35 Accordingly, in another aspect of the invention, there is provided the use of a surface active agent, preferably a scum reducing agent as herein before

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- described in a composition comprising a nitrogen containing compound selected from a polyamino-functional polymer, a dye fixing agent, and mixtures thereof, for reducing or preventing the formation of scum on fabrics or washing machine parts contacted with the composition. In other words, compositions which
- 5 comprise a nitrogenous compound as defined herein before but no scum reducing agent produce increased scum compared to the composition of the invention.

Process

- 10 The fabric softening composition can conveniently be made according to well known processes to the skilled person. An exemplary disclosure is given in EP-A-0,668,902.

- 15 The invention is illustrated in the following non limiting examples, in which all percentages are on a weight basis unless otherwise stated.

In the examples, the abbreviated component identifications have the following meanings:

DEQA	:	Di-(tallowyl-oxy-ethyl) dimethyl ammonium chloride
DOEQA	:	Di-(oleyloxyethyl) dimethyl ammonium methylsulfate
DTDMAC	:	Ditallow dimethylammonium chloride
DHEQA	:	Di-(soft-tallowyl-oxy-ethyl) hydroxyethyl methyl ammonium methylsulfate
Fatty acid	:	tallow fatty acid IV=18
Electrolyte	:	Calcium chloride
DTDMAMS	:	Ditallow dimethyl ammonium methylsulfate
SDASA	:	1:2 Ratio of stearyl dimethyl amine:triple-pressed stearic acid
Glycosperse S-20	:	Polyethoxylated sorbitan monostearate available from Lonza
Clay	:	Calcium Bentonite Clay, Bentonite L, sold by Southern Clay Products
TAE25	:	Tallow alcohol ethoxylated with 25 moles of ethylene oxide per mole of alcohol
PEG	:	Polyethylene Glycol 4000
PEI 1800 E1	:	Ethoxylated polyethylene imine (MW 1800, at 50% active) as synthesised in Synthesis example 1

- PEI 1800 E3 : Ethoxylated polyethylene imine (MW 1800, at 50% active) as synthesised as per Synthesis example 1
- PEI 1800 E7 AO : Amine oxide of ethoxylated polyethylene imine (MW 1800, at 50% active) as synthesised as per Synthesis example 4
- PEI 1200 E1 : Ethoxylated polyethylene imine (MW 1200, at 50% active in water) as synthesised in Synthesis example 5
- PEI 1200 E2 : Ethoxylated polyethylene imine (MW 1200, at 50% active in water) as synthesised per Synthesis example 5
- PEI 1200 E7 : Ethoxylated polyethylene imine (MW 1200, at 50% active in water) as synthesised per Synthesis example 5
- PEI 1200 E7 AO : Amine oxide of ethoxylated polyethylene imine (MW 1200, at 50% active) as synthesised as per Synthesis example 5 and 4
- Dye Fix 1 : Cellulose reactive dye fixing agent available under the tradename Tinofix FRD from Ciba-Geigy
- Dye Fix 2 : Cellulose reactive dye fixing agent available under the tradename Rewin DWR from CHT R. Beitlich

Scum reducing agent 1: N,N dimethyl-N-(2-hydroxyethyl)-N-dodecyl/tetradecyl ammonium bromide

Scum reducing agent 2: C12/C14 Choline ester

Scum reducing agent 3 : polyoxyalkylene alkyl amine commercially available from Akzo under the tradename Ethomeen T/15

Scum reducing agent 4 : polyoxyalkylene alkyl amine commercially available from Stepan under the tradename Secomine TA 15

Scum reducing agent 5 : polyoxyalkylene alkyl amine commercially available from Akzo under the tradename Ethoduomeen T/20

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LAS : Sodium linear C₁₂ alkyl benzene sulphonate

TAS : Sodium tallow alcohol sulphate

C25AS : Sodium C₁₂-C₁₅ linear alkyl sulphate

10

CxyEzS : Sodium C_{1x}-C_{1y} branched alkyl sulphate condensed with z moles of ethylene oxide

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	C45E7	:	A C ₁₄₋₁₅ predominantly linear primary alcohol condensed with an average of 7 moles of ethylene oxide
5	C25 E3	:	A C ₁₂₋₁₅ branched primary alcohol condensed with an average of 3 moles of ethylene oxide
	Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and a coconut oils.
	TFAA	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
10	TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
	Zeolite A	:	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ Si ₂ O ₂) ₁₂ · 27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers
15	Citric acid	:	Anhydrous citric acid
	Carbonate	:	Anhydrous sodium carbonate with a particle size between 200µm and 900µm
	Silicate	:	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O; 2.0 ratio)
	Sulphate	:	Anhydrous sodium sulphate
20	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm
	MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
25	CMC	:	Sodium carboxymethyl cellulose
	Savinase	:	Proteolytic enzyme of activity 4KNPU/g
	Carezyme	:	Cellulytic enzyme of activity 1000 CEVU/g
	Termamyl	:	Amylolytic enzyme of activity 60KNU/g
30	Lipolase	:	Lipolytic enzyme of activity 100kLU/g
	all sold by NOVO Industries A/S and of activity mentioned above unless otherwise specified		
	PB4	:	Sodium perborate tetrahydrate of nominal formula NaBO ₂ ·3H ₂ O·H ₂ O ₂
35	PB1	:	Anhydrous sodium perborate bleach of nominal formula NaBO ₂ ·H ₂ O ₂

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TAED : Tetraacetyl ethylene diamine
 DTPMP : Diethylene triamine penta (methylene phosphonate),
 marketed by Monsanto under the Trade name
 Dequest 2060

5 Photoactivated: Sulphonated Zinc Phthalocyanin encapsulated in
 bleach dextrin soluble polymer

Brightener : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5- triazin-
 2-yl)amino) stilbene-2:2'-disulphonate.

Silicone antifoam : Polydimethyldioxane foam controller with
 10 Siloxane-oxyalkylene copolymer as dispersing
 agent with a ratio of said foam controller to said
 dispersing agent of 10:1 to 100:1.

15 HEDP : 1,1-hydroxyethane diphosphonic acid

Bayhibit AM : 2-phosphonobutane-1,2,4-tricarboxylic acid commercially
 available from Bayer

TPTA : N,N'-Bis(3-aminopropyl)1,3-propanediamine commercially
 available from Aldrich

Synthesis Example 1 -Preparation of PEI 1800 E₁

Step A)-The ethoxylation is conducted in a 2 gallon stirred stainless steel
 autoclave equipped for temperature measurement and control, pressure
 20 measurement, vacuum and inert gas purging, sampling, and for introduction of
 ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set
 up to deliver ethylene oxide as a liquid by a pump to the autoclave with the
 cylinder placed on a scale so that the weight change of the cylinder could be
 monitored.

25 A 750 g portion of polyethyleneimine (PEI) (Nippon Shokubai, Epomin SP-018
 having a listed average molecular weight of 1800 equating to 0.417 moles of
 polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The
 autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg
 followed by pressurization with nitrogen to 250 psia, then venting to atmospheric
 30 pressure). The autoclave contents are heated to 130 °C while applying vacuum.
 After about one hour, the autoclave is charged with nitrogen to about 250 psia
 while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the
 autoclave incrementally over time while closely monitoring the autoclave

pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Step B)- The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

If a PEI 1800 E7 is desired, the following step of catalyst addition will be included between Step A and B.

Vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the

temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles).

Other preferred examples such as PEI 1800 E2, PEI 1800 E3, PEI 1800 E15 and PEI 1800 E20 can be prepared by the above method by adjusting the reaction time and the relative amount of ethylene oxide used in the reaction.

Synthesis Example 2 -4.7% Quaternization of PEI 1800 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1800 ethoxylated to a degree of 7 (224g, 0.637 mol nitrogen, prepared as in Synthesis Example 1) and acetonitrile (Baker, 150g, 3.65 mol). Dimethyl sulfate (Aldrich, 3.8g, 0.030 mol) is added all at once to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight. The acetonitrile is evaporated on the rotary evaporator at ~60°C, followed by a Kugelrohr apparatus (Aldrich) at ~80°C to afford ~220g of the desired material as a dark brown viscous liquid. A ¹³C-NMR (D₂O) spectrum shows the absence of a peak at ~58ppm corresponding to dimethyl sulfate. A ¹H-NMR (D₂O) spectrum shows the partial shifting of the peak at 2.5ppm (methylenes attached to unquaternized nitrogens) to ~3.0ppm.

Synthesis Example 3 -Oxidation of 4.7% Quaternized PEI 1800 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1800 which has been ethoxylated to a degree of 7, and ~4.7% quaternized with dimethyl sulfate (121.7g, ~0.32 mol oxidizable nitrogen, prepared as in Synthesis Example 2), hydrogen peroxide (Aldrich, 40g of a 50 wt% solution in water, 0.588 mol), and water (109.4g). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. A ¹H-NMR (D₂O) spectrum shows the total shifting of the methylene peaks at 2.5-3.0ppm to ~3.5ppm. To the solution is added ~5g of 0.5% Pd on alumina

pellets, and the solution is allowed to stand at room temperature for ~3 days. Peroxide indicator paper shows that no peroxide is left in the system. The material is stored as a 46.5% solution in water.

5 Synthesis Example 4 -Formation of amine oxide of PEI 1800 E₇

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added polyethyleneimine having a molecular weight of 1800 and ethoxylated to a degree of about 7 ethoxy groups per nitrogen (PEI-1800, E₇) (209 g, 0.595 mol nitrogen, prepared as in Synthesis Example I), and hydrogen peroxide (120 g of
10 a 30 wt % solution in water, 1.06 mol). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. ¹H-NMR (D₂O) spectrum obtained on a sample of the reaction mixture indicates complete conversion. The resonances ascribed to methylene protons adjacent to unoxidized nitrogens have shifted from the original position at ~2.5 ppm to ~3.5
15 ppm. To the reaction solution is added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for approximately 3 days. The solution is tested and found to be negative for peroxide by indicator paper. The material as obtained is suitably stored as a 51.1% active solution in water.

20 Synthesis Example 5 -Preparation of PEI 1200 E₁

Step A)-The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of
25 ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (having a listed average molecular weight of 1200 equating to about 0.625 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and
30 purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the
35 autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally

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over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Step B)- The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

If a PEI 1200 E7 is desired, the following step of catalyst addition will be included between Step A and B.

Vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions).

The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave

pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles).

Other preferred examples such as PEI 1200 E2, PEI 1200 E3, PEI 1200 E15 and PEI 1200 E20 can be prepared by the above method by adjusting the reaction time and the relative amount of ethylene oxide used in the reaction.

The corresponding amine oxide of the above ethoxylated PEI can also be prepared following synthesis Example 4.

Synthesis Example 6 -9.7% Quaternization of PEI 1200 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1200 ethoxylated to a degree of 7 (248.4g, 0.707 mol nitrogen, prepared as in Synthesis Example 5) and acetonitrile (Baker, 200 mL). Dimethyl sulfate (Aldrich, 8.48g, 0.067 mol) is added all at once to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight. The acetonitrile is evaporated on the rotary evaporator at ~60°C, followed by a Kugelrohr apparatus (Aldrich) at ~80°C to afford ~220g of the desired material as a dark brown viscous liquid. A ¹³C-NMR (D₂O) spectrum shows the absence of a peak at ~58ppm corresponding to dimethyl sulfate. A ¹H-NMR (D₂O) spectrum shows the partial shifting of the peak at 2.5ppm (methylenes attached to unquaternized nitrogens) to ~3.0ppm.

Synthesis Example 7-4.7% Oxidation of 9.5% Quaternized PEI 1200 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1200 which has been ethoxylated to a degree of 7, and ~9.5% quaternized with dimethyl sulfate (144g, ~0.37 mol oxidizable nitrogen, prepared as in Example 6), hydrogen peroxide (Aldrich, 35.4g of a 50 wt%

5 solution in water, 0.52 mol), and water (100g). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. A ^1H -NMR (D_2O) spectrum shows the total shifting of the methylene peaks at 2.5-3.0ppm to ~3.5ppm. To the solution is added just enough sodium bisulfite as a 40% water solution to bring the residual peroxide level down to 1-5ppm. The sodium sulfate which forms causes an aqueous phase to separate which contains salts, but little or no organics. The aqueous salt phase is removed and the desired oxidized polyethyleneimine derivative is obtained and stored as a 52% solution in water.

10

Example 1

The following compositions are in accordance with the present invention

Active (levels in %)	I	II	III	IV	V
Dye Fix 1	5.0	5.0	5.0	5.0	10.0
PEI 1200 E1	-	10.0	20.0	5.0	20.0
DEQA	-	-	-	-	-
Bayhibit AM	1.0	0.2	1.0	1.0	1.0
NH_4Cl	-	-	0.2	0.2	0.5
SRP2	-	-	-	0.5	1.0
MgCl_2	-	-	-	-	4.0
Brightener 1	-	-	-	-	0.2
Scum reducing agent 3	5	10	10	5	10
Water and minors to balance to 100					

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Example 2

The following compositions are in accordance with the present invention

Component	I	II	III	IV	V
Scum reducing agent 1	1.0	-	-	5.0	5.0
Scum reducing agent 2	-	-	-	2.5	2.5
Scum reducing agent 5	-	2.0	2.0	-	-
DEQA	2.6	18.0	19.0	-	-
TAE25	-	1.0	-	-	-
Fatty acid	0.3	1.0	-	-	-
Hydrochloride acid	0.02	0.02	0.02	-	-
PEG	-	0.6	0.6	-	-
Perfume	1.0	1.0	1.0	0.1	0.1
Silicone antifoam	0.01	0.01	0.01	-	-
PEI 1200 E4	3	3	-	15	-
TPTA	-		5	-	10
Dye fix 1	1.0	-	5.0	-	10
Dye fix 2	-	3	-	5.0	-
HEDP	0.2	-	-	0.4	-
Electrolyte (ppm)	-	600	1200	-	-
Dye (ppm)	10	50	50	-	-
Water and minors to balance to 100					

Component	VI	VII	VIII	IX
Scum reducing agent 4	2.5	5.0	10.0	1.0
DTDMAC	-	-	-	15
DEQA	2.6	19.0	-	-
TAE25	0.3	-	-	-
Fatty acid	0.3	-	-	-
Hydrochloride acid	0.02	0.02	-	0.02
PEG	-	0.6	-	0.6
Perfume	1.0	1.0	0.1	1.0
Silicone antifoam	0.01	0.01	-	0.01
PEI 1800 E4	3	3	10	3
Dye fix 1	1	3.0	10	1
Dye fix 2	2	-	-	2
Electrolyte (ppm)	-	600	-	600
Dye (ppm)	10	50	-	50
Water and minors to balance to 100				

Example 3

- 5 The following compositions for use as dryer-added sheets are in accordance with the invention

	I	II	III	IV	V	VI
Scum reducing agent 3	10.0	5.0	2.5	1.0	5.0	0.1
DOEQA	40	25	-	-	-	-
DHEQA	-	-	20	-	-	-
DTDMAMS	-	-	-	20	12	60
SDASA	30	30	20	30	20	-
Glycosperse S-20	-	-	10	-	-	-
Glycerol Monostearate	-	-	-	20	10	-
Clay	4	4	3	4	4	-

Perfume	0.7	1.1	0.7	1.6	2.6	1.4
PEI 1800 E1	-	5	-	-	-	-
PEI 1200 E4	-	-	4	2.2	-	-
PEI 1800 E4	2	-	-	-	5	7.0
Dye fix 1	2	5	4	2.2	5	3
HEDP	0.2	-	0.5	-	-	0.7
Glycolic	-	0.2	-	0.2	-	-
Polycarboxylic	-	0.2	-	-	0.4	-
Stearic acid to balance						

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Example 4

The following detergent formulations S and T, are in accordance with the present invention:

	S	T
Zeolite A	24.0	23.0
Sulphate	9.0	-
MA/AA	4.0	4.0
LAS	8.0	8.0
TAS	-	2.0
Silicate	3.0	3.0
CMC	1.0	0.4
Brightener	0.2	-
Soap	1.0	-
DTPMP	0.4	0.4
C45E7	2.5	2.0
C25E3	2.5	2.0
Silicone antifoam	0.3	5.0
Perfume	0.3	0.3
Carbonate	13.0	16.0
Citrate	-	5.0
PB4	18.0	-
PB1	4.0	14.0
TAED	3.0	6.0
Photoactivated bleach	0.02%	-
Savinase	1.0	1.0
Lipolase	0.4	0.4
Termamyl	0.30	0.6
Carezyme	-	0.6
PEI 1800 E7 AO	1.0	-
PEI 1200 E7 AO	-	1.0
Dye fix 1	2.0	1.0
Scum reducing agent 4	0.5	0.5
HEDP	0.2	-
Glycolic	-	0.2
Polycarboxylic	-	0.2

Balance (Moisture and Miscellaneous) to 100

Example 5

The following liquid detergent formulation, according to the present invention was prepared:

5

	U
C25AS	13
C25E3S	2
TFAA	6
C12-14 alkyl dimethylhydroxy ethyl ammonium chloride	1
Cationic ester	1.5
TPKFA	15
Citric acid	1
Ethanol	2
1,2 Propanediol	8
NaOH up to pH	7.5
DTPMP	1.2
Savinase	0.5
Termamyl (300 KNU/g)	0.15
Boric acid	1.5
Softening clay of the bentonite type	4
Suspending clay SD3	0.3
PEI 1200 E7	1
Dye fix 2	1
Scum reducing agent 5	0.2
Balance (Moisture and Miscellaneous)	100

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